Oxygen dependence of the magnetic order of Nd in $NdBa_2Cu_3O_{6+x}$

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Neutron scattering and specific heat measurements have been carried out on a series of $NdBa_2Cu_3O_{6+x}$ powder samples with varying oxygen concentrations ($x=0.94$, 0.78, 0.45, 0.3, 0.13) in order to study the effects of oxygen on the magnetic order of Nd. For our highest oxygenated superconducting $NdBa_2Cu_3O_{6.94}$ ($T_c\simeq 92$ K), three-dimensional (3D) long range order develops below $T_N\simeq 0.53$ K, with a spin configuration which is antiferromagnetic along all three crystallographic axes. For a small reduction of oxygen to $x=0.78$, we observe drastic effects on the Nd order; 3D order is inhibited and only short range 2D correlations are found at low temperature. However, the 2D correlations develop at a much higher temperature, near 1.5 K. At (nonsuperconducting) $x=0.45$, the 3D magnetic order is better developed at low temperature, yet long range order still does not occur. For $x=0.3$, 3D long range magnetic order of the Nd ions is reestablished, developing below $T_N\simeq 1.5$ K, three times that of the fully oxygenated material. All of these ordering temperatures are much higher than what is expected based on dipolar interactions alone, and this coupled with our experimental results indicates that exchange interactions play an essential role, and are strongly influenced by the chain layer oxygen.

The magnetic rare-earth order in $RBa_2Cu_3O_7$ (R = rare earth) has been studied in considerable detail for essentially all the magnetic rare earth ions.[1] Most of these systems are superconductors which display two-dimensional (2D) magnetic behavior and ordering temperatures near 1 K.[1] The effects of oxygen removal from the chain layer were at first believed to be inconsequential to the rare-earth order, as substitution of yttrium in $YBa_2Cu_3O_7$ by many of the rare-earth ions did not affect the superconducting properties, indicating that the rare-earth ions are electronically isolated from the Cu–O planes; and measurements on $GdBa_2Cu_3O_7$ and $GdBa_2Cu_3O_6$ indicated that the Gd ordering temperature was the same in the two systems. Therefore, specific heat and neutron scattering measurements on $NdBa_2Cu_3O_{6+x}$,[2] which showed a three-fold increase in the Nd ordering temperature in going from $NdBa_2Cu_3O_7$ ($T_N\simeq 0.5$ K) to $NdBa_2Cu_3O_{6.3}$ ($T_N\simeq 1.5$ K), came as a surprise.

In this article we report our most recent results from neutron scattering and specific heat measurements on the oxygen dependence of the magnetic order of Nd in powder samples of $NdBa_2Cu_3O_{6+x}$ ($x=0.94$, 0.78, 0.45, 0.3, 0.13). For our highest oxygenated superconducting $NdBa_2Cu_3O_{6.94}$ the Nd ions develop 3D long range magnetic order at $T_N\simeq 0.53$ K, with spins coupled antiferromagnetically along the a, b, and c directions.[2] The two experimental techniques at our disposal allow us to observe the manifestations of this long range magnetic order in two forms: a sharp specific heat anomaly, and resolution-limited magnetic Bragg peaks via neutron scattering. As we remove oxygen from this sample to arrive at partially de-oxygenated superconducting $NdBa_2Cu_3O_{6.78}$, long range order never develops down to the lowest temperatures achieved ($T=0.3$ K). Indeed, a rounded magnetic specific heat peak is observed, while neutron scattering reveals a broad, asymmetric lineshape to the magnetic scattering which we can model with a 2D theory assuming short range correlations. A further reduction of oxygen to insulating $NdBa_2Cu_3O_{6.45}$ does not restore long range order, though the magnetic scattering now indicates *both* 2D and 3D short range correlations which saturate near 1 K. With further reduction to $NdBa_2Cu_3O_{6.3}$, we find that long range order has been restored. However, we find that the ordering temperature is more than three times higher than for $NdBa_2Cu_3O_{6.94}$, increasing to $T_N\simeq 1.5$ K.

The neutron experiments were performed at the research reactor at the National Institute of Standards and Technology. The magnetic scattering data were taken with a wavelength of 2.35 Å, and a pyrolytic graphite monochromator and filter. Both a He^3 and He^3–He^4 dilution refrigerator were used for the low temperature measurements. A neutron profile refinement at a wavelength of 1.5453 Å and collimation of 10′-20′-10′ was also done to establish the oxygen stoichiometry of the powder. The preparation of the powder sample has been described in detail in a previous article.[2] The superconducting transition for $NdBa_2Cu_3O_{6.94}$ was $T_c\simeq 92$ K, while that of $NdBa_2Cu_3O_{6.78}$ was $T_c\simeq 63$ K.

The anisotropy of the $RBa_2Cu_3O_{6+x}$ unit cell, where $c\simeq 3a$, lends itself to 2D behavior for the rare earths since there is just one rare earth atom per chemical unit cell. This has been clearly demonstrated in $DyBa_2Cu_3O_7$ and $ErBa_2Cu_3O_7$, where above their 3D ordering temperatures only 2D magnetic correlations are observed.[3] Therefore, for Nd we also expect the diffuse scattering above T_N to display dominantly 2D behavior. In Fig. 1(a) we show a scattering profile just above the ordering temperature for $NdBa_2Cu_3O_{6.94}$. The solid curve is a least-squares fit to a

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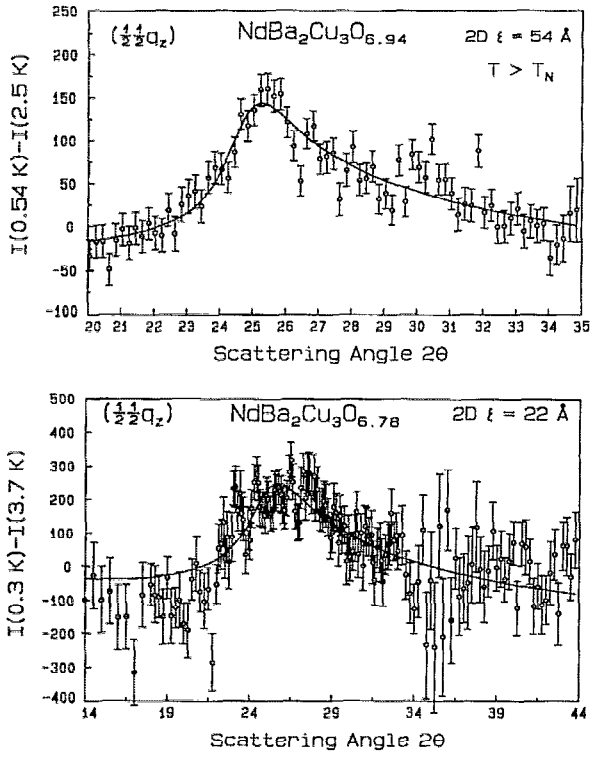

FIG. 1. (a) Angular scan through the diffuse magnetic scattering just above the ordering temperature in $NdBa_2Cu_3O_{6.94}$. The solid curve is a fit to a 2D model which assumes a rod of scattering characterized by the 2D wave vector $(\frac{11}{22})$. (b) A similar scan made at low temperature on partially de-oxygenated superconducting $NdBa_2Cu_3O_{6.78}$. For this oxygen concentration the magnetic scattering remains diffusive down to low temperature even though the scattering intensity has already saturated. The fitted 2D correlation length is only $\xi \simeq 22$ Å.

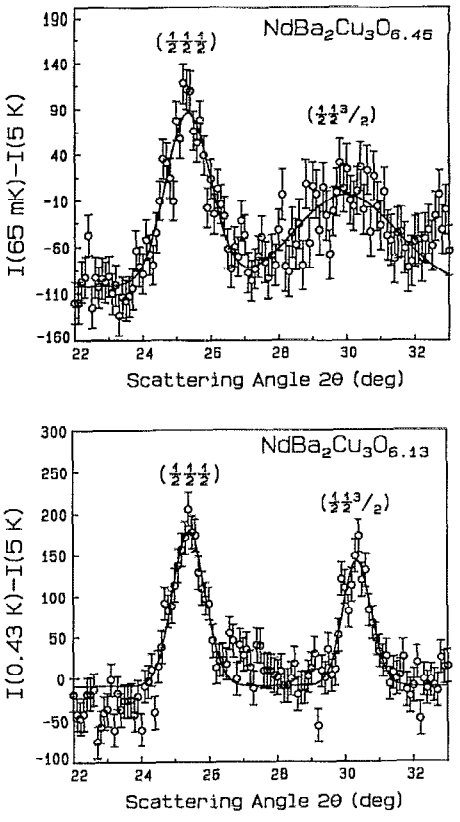

FIG. 2. (a) Low temperature angular scan through two 3D magnetic peaks indexed as $(\frac{111}{222})$ and $(\frac{113}{222})$, on the insulating $NdBa_2Cu_3O_{6.45}$ sample. The 3D correlations are still only short range in nature, though they are considerably stronger than observed in $NdBa_2Cu_3O_{6.78}$. (b) A similar scan taken on $NdBa_2Cu_3O_{6.13}$ shows sharp resolution-limited magnetic Bragg peaks, indicating that 3D long range order is restored for this oxygen concentration.

2D model, which assumes there is a rod of magnetic scattering characterized by the 2D wave vector $(\frac{11}{22})$. To generate the fitted curve we use Warren's approach[4] of averaging the scattered intensity for a 2D powder over all possible orientations of reciprocal space, but here we assume a Lorentzian shape to the 2D rod of scattering rather than Gaussian as assumed in his case. This is appropriate for diffuse magnetic scattering where the 2D rod is proportional to the spin–spin correlation function, which in the Ornstein–Zernike approximation is given by

$$\langle S(-\mathbf{Q})S(\mathbf{Q})\rangle - \langle S(-\mathbf{Q})\rangle\langle S(\mathbf{Q})\rangle \sim (Q^2+\kappa^2)^{-1}, \tag{1}$$

where κ $(=1/\xi)$ is the 2D inverse correlation length. We then get for the scattering intensity

$$I_{hk} = \text{const} \times \frac{|F_M|^2}{\sin\theta} F(\theta), \tag{2}$$

where

$$F(\theta) = \int_0^{\pi/2} \pi\kappa^2 \left(\frac{16\pi^2}{\lambda^2} (\sin\theta\cos\phi - \sin\theta_{hk})^2 + \kappa^2 \right)^{-1/2} d\phi, \tag{3}$$

$2\theta_{hk}$ is the scattering angle where the Ewald sphere first intercepts the rod, 2θ is the scattering angle, λ is the neutron wavelength, and F_M is the magnetic structure factor for the 2D magnetic unit cell.[5] The fit in Fig. 1(a) is very good, indicating just above T_N that the 2D correlations are strong. This does not rule out the possibility of there being weak 3D correlations above T_N, as it is difficult to resolve the 3D correlations in this type of measurement. Also shown in Fig. 1 is a measurement taken on our partially de-oxygenated superconducting sample $NdBa_2Cu_3O_{6.78}$, where we have put the two sets of data together for comparison. Figure 1(b) is a scan taken at low temperature on this powder, and the solid curve is a least squares fit to Eq. (2). Quite unexpectedly we find that at low temperature, where the magnetic scattering has already saturated, it is still *only* short range in nature, arising from 2D short range magnetic correlations. The 2D correlation length we extract at $T=0.3$ K is only 22 Å, as compared to $NdBa_2Cu_3O_{6.94}$ where we found, just above T_N at $T=0.54$ K, $\xi_{2D} \simeq 54$ Å. Of course, below T_N our highest oxygenated sample displays 3D long range order.

A low temperature scan taken on the insulating $NdBa_2Cu_3O_{6.45}$ sample is shown in Fig. 2(a), where we can now clearly resolve two peaks at the 3D Bragg positions $(\frac{111}{222})$ and $(\frac{113}{222})$. At this temperature the scattering intensity has already saturated, yet the two peaks are still considerably broader than the resolution. This indicates

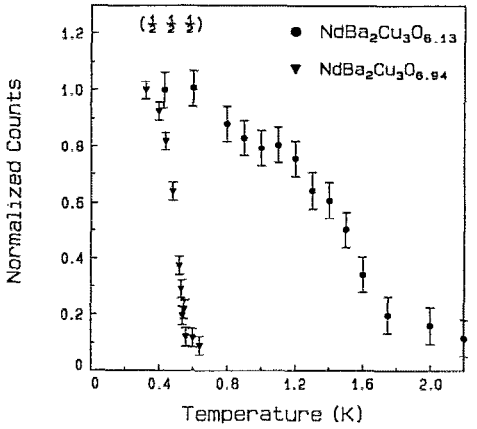

FIG. 3. Temperature dependence of the magnetic scattering intensity measured at the 3D Bragg position $(\frac{111}{222})$ for both $NdBa_2Cu_3O_{6.94}$ and $NdBa_2Cu_3O_{6.13}$. The ordering temperature for $NdBa_2Cu_3O_{6.13}$ ($T_N \simeq 1.75$) is more than three times higher than that in $NdBa_2Cu_3O_{6.94}$ ($T_N \simeq 0.53$ K).

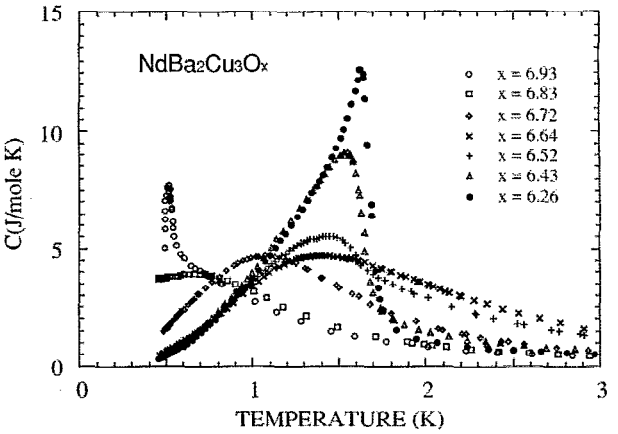

FIG. 4. Magnetic specific heat C vs temperature for the range of oxygen concentration $0.26 \lesssim x \lesssim 0.93$ from Ref. 6.

that the 3D correlations are considerably stronger than what we observed in $NdBa_2Cu_3O_{6.78}$, but 3D long range order is still absent. Also in this figure we show the same scan taken on our sample with lowest oxygen stoichiometry $NdBa_2Cu_3O_{6.13}$ at low temperatures. The important difference is that in Fig. 2(b) the two peaks are resolution-limited magnetic Bragg peaks. The relative intensities of the $(\frac{111}{222})$ and $(\frac{113}{222})$ peaks differ from what we observed for the same peaks in $NdBa_2Cu_3O_7$,[2] where $\mu \| c$. In fact, for $NdBa_2Cu_3O_{6.13}$ and $NdBa_2Cu_3O_{6.3}$ we can model the data very well if we assume the moment direction is off the c axis by 45°. We also find the ordered moment to be slightly reduced by about 20% from what we estimate for $NdBa_2Cu_3O_7$, where $\langle \mu^z \rangle \simeq 1.1 \mu_B$.[2] However, the Nd ordering in the insulating phase could be complicated by the Cu order, and may account for these differences. In Fig. 3 we show the temperature dependence of the magnetic scattering measured at the $(\frac{111}{222})$ position for two different oxygen concentrations, $NdBa_2Cu_3O_{6.13}$ and $NdBa_2Cu_3O_{6.94}$. From the figure we see that the transition temperatures differ by about a factor of three, where for $NdBa_2Cu_3O_{6.13}$ we find $T_N \simeq 1.75$ K and for $NdBa_2Cu_3O_{6.94}$ $T_N \simeq 0.53$ K.

In Fig. 4 we show previously published magnetic specific heat $C(T)$ data taken over the range of oxygen concentration $0.26 \lesssim x \lesssim 0.93$.[6] For $NdBa_2Cu_3O_{6.93}$ we observe a sharp specific heat anomaly near 0.5 K, in agreement with the neutron results.[2] As oxygen is removed we observe a rounded peak in $C(T)$, although as more oxygen is removed the peak gets somewhat sharper and occurs at a progressively higher temperature. At $x \simeq 0.3$, the anomaly is again very sharp, and the transition is at the relatively high temperature of $T \simeq 1.75$ K, again in excellent agreement with the neutron results. Hence, both experimental techniques show the same striking oxygen dependence to the magnetic ordering.

The ordering temperatures for both the fully oxygenated sample and the de-oxygenated sample are considerably higher than expected based on dipole interactions alone. In view of our results, as well as the inability of dipole interactions to yield such high ordering temperatures, we believe there must be an additional rare-earth magnetic interaction involving the chain layer oxygen. It is not clear to us how such a mechanism would work though, as the rare-earth ions are displaced further from the chain layer than any other atom in the unit cell. An additional effect could arise from the Cu order, though it is generally not believed to affect the rare-earth order. However, Mössbauer experiments[7] on $ErBa_2Cu_3O_6$ and $YbBa_2Cu_3O_6$ have indicated that an anomalous Cu molecular field arises at the rare-earth site. In the superconducting phase the short range Cu fluctuations may be inducing similar behavior at the rare-earth site as we see in our partially de-oxygenated superconducting samples of $NdBa_2Cu_3O_{6+x}$, while in the insulating phase the Cu orders, again inducing similar rare-earth behavior.

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